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54 Use of titanium and zirconium compounds as homogeneous catalyst and novel titanium and zirconium compounds.

57 The use of chelating bisphenoxide and binaphtoxide titanium and zirconium compounds as homogeneous catalysts in the polymerization and oligomerization of unsaturated hydrocarbons, in particular the polymerizations of olefinically unsaturated compounds and the cyclic trimerization of terminal acetylenes, is described.
Furthermore, certain novel chelating silyl containing binaphtoxide titanium and zirconium compounds are described.

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The present invention relates to the use of titanium and zirconium compounds having chelating alkoxide ligands as homogeneous catalysts for olefin polymerization or oligomerization, including the cyclic trimerization of terminal acetylenes, and to novel titanium and zirconium compounds having chelating alkoxide ligands containing silyl groups.

From U.S. patent No. 4,452,914 a titanium complex or compound is known, which may be used as the transition metal component in Ziegler-Natta catalysts. Said titanium complex or compound is obtained by reacting a titanium compound of general formula $Ti(OR)_nX_{4-n}$, wherein R represents a hydrocarbyl group of 1 to 20 carbon atoms, X represents a halogen and n is an integer having a value of 0 to 4, with at least one compound containing at least one hydroxyl group. This latter compound includes optionally substituted bisphenol compounds and optionally substituted binaphthol compounds, wherein two aromatic rings may be linked via a divalent bridging group, such as e.g. a hydrocarbyl group or a sulphur containing group. Said U.S. patent however, does not describe the presence of silyl groups as substituents on the aromatic rings of the compounds containing at least one hydroxyl group.

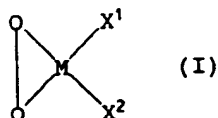
From European Patent Application No. 0,433,943 a catalyst for preparing 1,4-polybutadiene is known comprising a transition metal compound, an organoaluminium compound and an organic compound having at least two hydroxyl groups. This organic compound may be an optionally substituted bisphenol or binaphthol compound, wherein the aromatic rings containing the hydroxyl groups may be connected through a divalent bridging group, such as a hydrocarbyl group or a sulphur containing group. However, said European patent application is silent about the use as an olefin polymerization or oligomerization catalyst, while the presence of silyl substituents on the hydroxy containing aromatic rings is not disclosed either.

U.S. Patent No. 4,798,903 discloses optically active 3,3'-disilylbinaphthol derivatives, which are useful as ligands. More specifically, said 3,3'-disilylbinaphthol derivatives are described to be useful for reacting with tri-alkyl aluminium, thus obtaining active aluminium reagents, which are useful as catalysts for the asymmetric hetero Diels-Alder reaction in the reactions between aldehydes and conjugated dienes. In general, the 3,3'-disilylbinaphthol compounds are described to be useful as ligands of optically active catalysts. However, their use as olefin polymerization or oligomerization catalysts is not described, while complexes with zirconium or titanium compounds are not described either.

Hence, until now the use of titanium or zirconium compounds having chelating bisphenol or binaphthol ligands as homogeneous catalysts in the polymerization or oligomerization of olefinically unsaturated compounds as well as in the cyclic trimerization of terminal acetylenes was not known. In addition hereto, titanium and zirconium compounds having chelating 3,3'-disilylbinaphthol ligands were also not known.

Therefore it is an object of the present invention to provide improved homogeneous catalysts for the polymerization or oligomerization of olefinically unsaturated compounds and terminal acetylenes.

Accordingly, the present invention relates to a process for the polymerization or oligomerization of olefinically or acetylenically unsaturated hydrocarbons in the presence of a homogeneous catalyst characterized in that the latter is a compound of general formula (I)

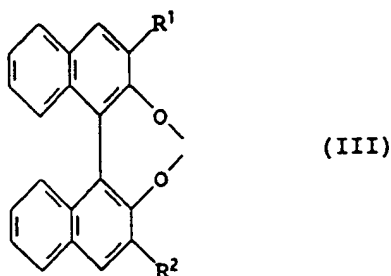
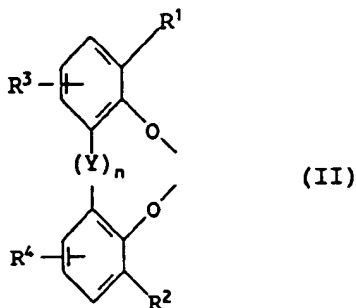


wherein:

- M is Ti or Zr;
- X¹ and X² independently represent halogen, an optionally substituted aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms, a silyl group or an alkoxy group of general formula -OR' with R' being an aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms;



represents a chelating alkoxide ligand of general formula (II) or (III):



wherein:

- 30
- R¹ and R² independently represent a sterically hindering alkyl group or an alkoxy group of general formula OR' with R' as previously defined, or a silyl group of general formula SiR^aR^bR^c with R^a, R^b and R^c independently representing a lower alkyl group, an aryl group, an arylalkyl group or an alkylaryl group;
 - R³ and R⁴ independently represent hydrogen, an optionally substituted aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms, a silyl group or an alkoxy group of general formula OR' with R' as previously defined;
 - 35 - Y is a divalent bridging group selected from the group consisting of methylene, ethylene, -S- and -O-; and
 - n is 0 or 1.

The said homogeneous catalysts are particularly useful in the polymerization or oligomerization of ethene, propene or hexene, while the best results are achieved in the polymerization or oligomerization of ethene. The term "olefinically unsaturated hydrocarbon" wherever used in this specification should be interpreted wide enough as to comprise both mono-unsaturated compounds as well as diolefinically unsaturated compounds. From the latter group of compounds 1,3-butadiene can be cited as example. The mono-olefins can have terminal unsaturation (alpha-olefins) or internal unsaturation as in e.g. 2-hexene or 3-hexene.

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On the other hand, the said titanium and zirconium compounds may also be effectively used as homogeneous catalysts in the oligomerization of terminal acetylenes and more particularly in the cyclic trimerization of terminal acetylenes. Preferably, said acetylenes have the general formula (IV):

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wherein R represents a hydrocarbyl silyl group, an optionally substituted aryl group or an alkyl group of 1 to 20 carbon atoms other than tertiary alkyl. In an even more preferred embodiment, said group R is selected from the group consisting of trimethyl silyl, phenyl and p-tolyl.

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The polymerization or oligomerization is effected by methods known per se, it can be carried out in bulk, in solution, in slurry or in gasphase reaction. Usual temperatures will be in the range of from 95 to 150 °C, the pressure will normally range from 1 to 100 bar, preferably from 3 to 70 bar.

It is preferred that the groups X¹ and X² as depicted in formula (I) are the same and selected from the group consisting of halogen, alkylene trialkyl silyl, aryl, alkylaryl, arylalkyl and lower alkyl. From this group of preferred substituents chlorine, benzyl, methylene trimethyl silyl and methyl are the most preferred members.

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If the chelating alkoxide ligand is the one represented by general formula (II), n may be either 0 or 1, whereby in the event n equals 1, it is preferred that Y is a methylene group or -S-. In addition hereto, it is also preferred

that R¹ and R² are the same and represent a bulky alkyl group of 1 to 10 carbon atoms, preferably tertiary butyl. The other substituents R³ and R⁴ are preferably both located on the meta-position in relation to R¹ and R² respectively, while in such a case it is preferred that R³ and R⁴ are the same and represent methoxy, methyl or ethyl.

5 Particularly preferred are 2,2'-(4-OMe,6-tBuC₆H₂O)₂Ti(CH₂Ph)₂,

2,2'-S(4-Me,6-tBuC₆H₂O)₂Ti(CH₂Ph)₂ and

2,2'-CH₂(4-Et,6-tBuC₆H₂O)₂Ti(CH₂Ph)₂, whereby

2,2'-S(4-Me,6-tBuC₆H₂O)₂Ti(CH₂Ph)₂ is most preferred for use as olefin polymerization catalyst.

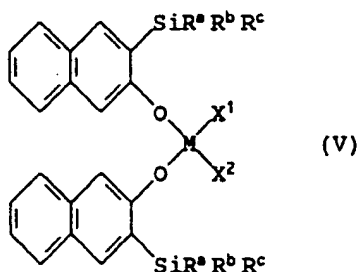
10 If, however, the chelating alkoxide ligand is the one represented by general formula (III), it is preferred that R¹ and R² both represent a silyl group of general formula SiR^aR^bR^c with R^a, R^b and R^c independently representing a lower alkyl group, an aryl group, an arylalkyl group or an alkylaryl group. In such a case, it is preferred that R¹ and R² are selected from trimethyl silyl, diphenyl methyl silyl, triphenyl silyl and dimethyl phenyl silyl, with R¹ and R² preferably being the same.

The present invention also relates to novel compounds of general formula (V):

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wherein:

- M is Ti or Zr;
- 30 - X¹ and X² independently represent halogen, an optionally substituted aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms, a silyl group or an alkoxy group of general formula -OR' with R' being an aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms; and
- R^a, R^b and R^c independently represent a lower alkyl group, an aryl group, an arylalkyl group or an alkylaryl group, of which methyl and phenyl are preferred.

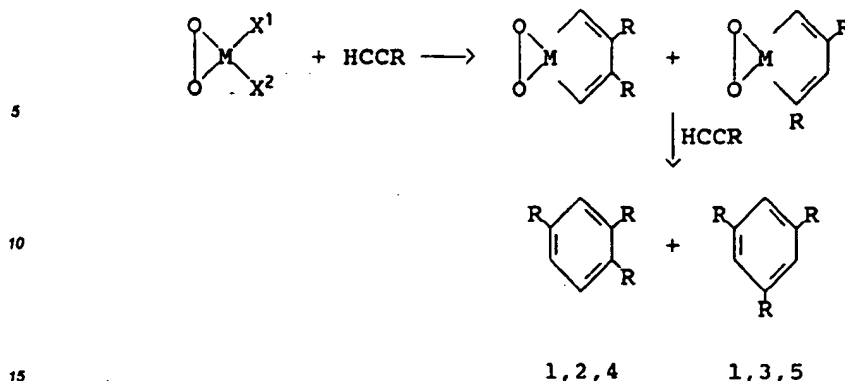
35 In a preferred embodiment of the present invention X¹ and X² are the same and selected from the group consisting of halogen, alkylene trialkyl silyl, aryl, alkylaryl, arylalkyl and lower alkyl, while from this group chlorine, benzyl, methylene trimethyl silyl and methyl are the most preferred members.

Preferred novel compounds are those of formula V wherein either R^a, R^b and R^c are selected from methyl and phenyl, or wherein M=Zr or Ti, R^a=R^b=R^c=independently methyl or phenyl and X¹=X²=C1 or benzyl, or methyl, or wherein M=Zr, R^a=R^b=R^c=phenyl and X¹=X²=methylene trimethyl silyl.

40 If chelating alkoxide titanium and zirconium compounds as described hereinbefore are used as homogeneous catalyst for the polymerization of olefins such as ethene and propene, a cocatalyst is required for activating the catalyst. In principle, any cocatalyst known in the art can be used, but it is preferred to use an organoaluminum compound, such as diethylaluminum chloride or methylaluminoxane. The best results however, are obtained when using methylaluminoxane.

45 When used as catalyst in the cyclic trimerization of terminal acetylenes to yield benzenes, the catalyst needs no activation by means of a cocatalyst due to the presence of the terminal triple bond and the resulting acidic character of the terminal hydrogen atom in combination with the basic character of the bonding between the titanium or zirconium atom and the X¹ and X² group. This also explains why H-C≡C-tAlkyl and internal acetylenes do not undergo the cyclic trimerization reaction: H-C≡C-tAlkyls are only very weakly acidic, while internal acetylenes such as e.g. but-2-yne are not acidic at all due to the absence of an acidic hydrogen atom which is directly bonded to the C≡C entity. The cyclic trimerization reaction proceeds as follows:

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The symmetric 1,3,5-trisubstituted benzene is disfavoured for more bulkier binaphthol or bisphenol ligands, i.e. binaphthol and bisphenol ligands having bulky X¹ and X² groups. Consequently, the ratio of 1,2,4-trisubstituted benzene to its 1,3,5-isomer can be controlled by the nature of the X¹ and X² groups bonded to the metal atom.

The invention is further illustrated by the following examples, however without restricting the invention to these specific embodiments.

Examples

All experiments for preparing the chelating alkoxide titanium and zirconium compounds were performed in an argon atmosphere using Schlenk type glassware or in a Braun single station dry-box equipped with a -40 °C fridge under a nitrogen atmosphere (Schlenk and Braun are trade marks).

Nuclear Magnetic Resonance (NMR) spectra were recorded on Varian XL-200, Varian VXR-300 or Bruker-500 MHz spectrometers (Varian and Bruker are trade marks). Chemical shifts (δ) are reported in parts per million and referenced to the residual protons in deuterated solvents. Coupling constants J_{AB} are reported in hertz (Hz). Solvents were P.A. grade and were dried over sodium wire, then distilled from the appropriate drying reagent (sodium benzophenone ketyl for ether and THF, sodium for hexane and toluene) under argon prior to use. Deuterated solvents were dried over 4 Ångstrom molecular sieves.

Binaphthol and bisphenol ligands were prepared according to methods described in J. Org. Chem. 1981, 46, 393; Bull. Chem. Soc. Japan 1988, 61, 2975; Tet. Lett. 1983, 24, 5611; J. Chem. Soc., C 1971, 1750 and J. Org. Chem. 1983, 48, 4948.

Zr(CH₂Ph)₂Cl₂ and M(CH₂Ph)₄ (M=Ti, Zr) were prepared according to the methods described in J. Organomet. Chem. 1981, 205, 319 and J. Organomet. Chem. 1971, 26, 357.

Melting points of the polymers were determined by Differential Scanning Calorimetry (DSC).

Example 1

(1,1'-(2,2',3,3'-OC₁₀H₆SiMe₃)₂)ZrCl₂ - which corresponds to the compound of formula (V) wherein M=Zr, R^a=R^b=R^c=methyl and X¹=X²=Cl- was prepared as follows.

0.494 g (1.18 mmol) Zr(CH₂Ph)₂Cl₂ was dissolved in 5 ml toluene at 25 °C. To this solution was added 0.338 g (1.18 mmol) 3,3'-bis(trimethylsilyl)-1,1'-bi-2,2'-naphthol dissolved in 5 ml toluene. After stirring for 16 hours at 20 °C the toluene was removed in vacuo and the red-brown powder was washed with hexane. Recrystallization from an ether/hexane 1:1 mixture at -40 °C afforded a yellow powder. Yield: 0.383 g, corresponding to 73%.

¹H NMR (C₆D₆, 25 °C): δ 8.10 (s, 2H); 7.8-7.7 (d, 2H); 7.2-6.95 (m, 4H); 6.86-6.75 (m, 2H); 0.70 (s, 18H, SiMe₃)
¹³C NMR (C₆D₆): δ 158.1; 135.7; 129.6; 128.4; 128.3; 128.2; 125.7; 124.7; 123.6; 111.4; -0.58 (SiMe₃)

Analysis for $C_{26}H_{28}O_2Si_2Cl_2Zr$:					
Calculated:	C, 52.86;	H, 4.78;	Si, 9.51;	Cl, 12.00;	Zr, 15.44
Found :	C, 53.12;	H, 5.04;	Si, 9.20;	Cl, 11.86;	Zr, 15.30

Example 2

(1,1'-(2,2',3,3'-OC₁₀H₆SiMePh₂)₂)ZrCl₂ -which corresponds to the compound of formula (V) wherein M=Zr, R^a=methyl, R^b=R^c=phenyl and X¹=X²=Cl- was prepared in a similar manner as described in Example 1.

¹H NMR (C₆D₆, 25°C): δ 7.75 (br, 6H); 7.62 (d, 2H); 7.52 (d, 2H); 7.43 (m, 6H); 7.27 (m, 6H); 7.17 (t, 2H); 7.06 (t, 2H); 6.73 (d, 2H); 1.17 (s, 6H, Me)

Analysis for $C_{48}H_{38}O_2Si_2Cl_2Zr$:					
Calculated:	C, 65.76;	H, 5.08;	Si, 6.15;	Cl, 7.76;	Zr, 9.99
Found :	C, 65.58;	H, 5.14;	Si, 6.19;	Cl, 8.00;	Zr, 10.10

Example 3

(1,1'-(2,2',3,3'-OC₁₀H₆SiPh₃)₂)ZrCl₂ -which corresponds to the compound of formula (V) wherein M=Zr, R^a=R^b=R^c=phenyl and X¹=X²=Cl- was prepared in a similar manner as described in Example 1.

¹H NMR (C₆D₆/d⁴-THF, 25 °C): δ 8.07 (s, 2H); 8.0 (m, 12H); 7.35 (d, 2H); 7.25-7.15 (m, 18H); 7.35 (d, 2H); 6.86 (t, 2H, 7.7 Hz); 6.75 (t, 2H, 7.7 Hz)

¹³C NMR (C₆D₆): δ 160.2; 142.1; 137.1; 137.0; 135.5; 129.9; 129.8; 128.8; 127.4; 126.8; 124.5; 124.0; 117.9

Analysis for $C_{58}H_{40}O_2Si_2Cl_2Zr$:					
Calculated:	C, 69.47;	H, 4.86;	Si, 5.41;	Cl, 6.48;	Zr, 8.79
Found :	C, 69.22;	H, 5.04;	Si, 5.30;	Cl, 6.69;	Zr, 8.61

Example 4

(1,1'-(2,2',3,3'-OC₁₀H₆SiMe₃)₂)Ti(CH₂Ph)₂ -which corresponds to the compound of formula (V) wherein M=Ti, R^a=R^b=R^c=methyl and X¹=X²=benzyl- was prepared as follows.

To 0.153 g (0.371 mmol) Ti(CH₂Ph)₄ dissolved in 10 ml toluene and cooled to -40 °C was added 0.16 g (0.372 mmol) (HOC₁₀H₆SiMe₃)₂. The solution was allowed to warm to 20 °C with stirring and was stirred at this temperature for 15 hours. The toluene was removed in vacuum to afford a red oil, which was recrystallized to give the solid product.

¹H NMR (C₆D₆, 25 °C): δ 8.17 (s, 2H); 7.2-6.8 (m); 2.87 (2H, AB, CH₂); 2.35 (AB, 2H, CH₂); 0.48 (s, 18H, SiMe₃)

Example 5

(1,1'-(2,2',3,3'-OC₁₀H₆SiMePh₂)₂)Zr(CH₂Ph)₂ -which corresponds to the compound of formula (V) wherein M=Zr, R^a=methyl, R^b=R^c=phenyl and X¹=X²=benzyl- was prepared analogous to Example 4 using Zr(CH₂Ph)₄.

Example 6

(1,1'-(2,2',3,3'-OC₁₀H₆SiPh₃)₂)Ti(CH₂Ph)₂ -which corresponds to the compound of formula (V) wherein M=Ti, R^a=R^b=R^c=phenyl and X¹=X²=benzyl- was prepared analogous to Example 4.

¹H NMR (C₆D₆, 25 °C): δ 8.33 (s, 2H); 8.0-7.92 (m, 12H); 7.2-6.8 (m + C₆D₆H); 6.75 (m, 4H); 6.45 (m, 4H); 1.4 (AB, J_{AB} = 11 Hz, 2H, CH₂); 1.05 (AB, J_{AB} = 11 Hz, 2H, CH₂)

Analysis for $C_{70}H_{54}O_2Si_2Ti$:			
Calculated:	C, 81.53;	H, 5.28;	Ti, 4.64
Found :	C, 81.24;	H, 5.41;	Ti, 4.75

Example 7

- (1,1'-(2,2',3,3'-OC₁₀H₆SiPh₃)₂)ZrMe₂(ether)₂ - which corresponds to the compound of formula (V) wherein M=Zr, R^a=R^b=R^c=phenyl and X¹=X²=methyl- was prepared as follows. 0.896 g (0.83 mmol) (C₁₁H₆OSiPh₃)₂ZrCl₂.toluene was suspended in 60 ml ether in a small Schlenk tube. This was cooled to -40 °C and 2 equivalents MeLi (1.04 ml of 1.6 M solution) in ether were added dropwise. After 10 minutes the orange suspension became a clear yellow solution and then began to turn cloudy. The solution was filtered, concentrated under vacuum and crystallized at -40 °C to give a white crystalline solid.
- ¹H NMR (C₆D₆, 25 °C): δ 8.28 (s, 2H); 7.92 (m); 7.53 (m); 7.16 (m); 6.97 (m); 3.14 (q, 8H, ether); 0.78 (t, 12H, ether); -0.136 (s, 6H, Me) 6.75 (t, 2H, 7.7 Hz)
- ¹³C NMR (C₆D₆): δ 159.86; 142.0 (d, 149 Hz); 138.2; 136.2; 129.3; 127.1; 125.8; 123.3; 118.2; naphthyl and phenyl resonances: 66.1 (t, 141 Hz, ether); 46.04 (q, 118 Hz, Me); 14.22 (q, 129 Hz, ether)

Analysis for C ₆₈ H ₄₀ O ₂ Si ₂ Cl ₂ Zr:					
Calculated:	C, 74.48;	H, 5.21;	Zr, 8.33		
Found :	C, 74.75;	H, 5.32;	Zr, 8.60;	Li, 0.0;	Cl<0.2

Example 8

- (1,1'-(2,2',3,3'-OC₁₀H₆SiPh₃)₂)Zr(CH₂Ph)₂ - which corresponds to the compound of formula (V) wherein M=Zr, R^a=R^b=R^c=phenyl and X¹=X²=benzyl- was prepared as follows.
- To 0.795 g (1.74 mmol) Zr(CH₂Ph)₄ dissolved in 30 ml toluene was added 1.4 g (1.74 mmol) 3,3'-bis(tri-phenylsilyl)-1,1'-bi-2,2'-naphthol. After stirring for 16 hours at 20 °C the toluene was removed in vacuo. The resulting yellow oil was washed with hexane to give a yellow powder. Yield: 1.70 g, corresponding to 91%.
- ¹H NMR (CD₂Cl₂, 25 °C): δ 8.15 (s, 2H); 7.75 (d, 2H); 7.65 (m, 10H); 7.35 (m, 24H); 6.78 (d, 2H); 6.55 (m, 6H); 5.70 (d, 4H, benzyl H_o); 0.88 (AB, 2H, 9.8 Hz); 0.64 (AB, 2H, 9.8 Hz)
- ¹³C NMR (CD₂Cl₂): δ 157.7; 143.9; 138.9; 137.5; 137.1; 134.9; 130.9; 130.0; 129.9; 128.3; 128.1; 127.5; 127.1; 125.9; 124.6; 124.3; 116.1; 68.1 (t, C_{H2}, J_{CH} = 133 Hz)

Example 9

- (1,1'-(2,2',3,3'-OC₁₀H₆SiPh₃)₂)Zr(CH₂SiMe₃)₂ - which corresponds to the compound of formula (V) wherein M=Zr, R^a=R^b=R^c=phenyl and X¹=X²=methylene trimethyl silyl- was prepared analogous to Example 8.
- ¹H NMR (CD₂Cl₂, 25 °C): δ 8.35 (s, 2H); 8.0-7.92 (m, 12H); 7.2-6.8 (m + C₆D₅H); 7.15 (d, 2H); 0.5 (AB, 2H, CH₂); -0.50 (AB, 2H, CH₂); -0.4 (s, 18H, SiMe₃)
- ¹³C NMR (CD₂Cl₂): δ 156.0; 142.9; 137.3; 137.0; 130.1; 130.0; 128.8; 128.7; 128.4; 128.0; 127.0; 126.1; 124.4; 117.2 (phenyl and phenyl resonances); 67.6 (CH₂); 1.3 (SiMe₃)

Example 10

- In this example the use of several chelating alkoxide titanium and zirconium catalysts in the polymerization of ethene and propene is illustrated.

Preparation of 2,2'-S(4-Me,6-tBuC₆H₂O)₂Ti(CH₂Ph)₂(Cat 1)

- This compound corresponds to Formula (I) with X¹=X²=benzyl having as the alkoxide ligand the ligand of formula (II), wherein n=1, Y=S-, R¹=R²=tertiary butyl and R³=R⁴=methyl.

0.21 g 2,2'-S(4-Me,6-tBuC₆H₂OH)₂ dissolved in 2 ml toluene was added to a cooled (-20 °C) solution of 0.24 g (0.583 mmol) Ti(CH₂Ph)₄ in 3 ml toluene/5 ml hexane. The red purple solution was stirred for 1 hour at 20 °C and the solvent was removed under vacuum. Extraction with hexane gave a dark red, very hexane soluble, slightly oily product. Recrystallization from hexane yielded analytically pure Cat 1.

Preparation of 2,2'-CH₂(4-Et,6-tBuC₆H₂O)₂Ti(CH₂Ph)₂ (Cat 2)

This compound corresponds to Formula (I) with X¹=X²=benzyl having as the alkoxide ligand the ligand of formula (II), wherein n=1, Y=methylene, R¹=R²=tertiary butyl and R³=R⁴=ethyl.

81 mg (0.20 mmol) Ti(CH₂Ph)₄ in 5 ml hexane was cooled to -40 °C and then added to a suspension of 72 mg (0.20 mmol) of 2,2'-bis(3-t-butyl-5-ethylphenol) in 5 ml hexane, also cooled to -40 °C. After addition at -40 °C the suspension was allowed to warm slowly to 20 °C. After stirring for 2 hours at 20 °C the resulting red coloured solution stripped under vacuum to give a red foam. Crystallization of a concentrated hexane solution at -40 °C gave micro-crystalline Cat 2.

Preparation of 2,2'-(4-OMe,6-tBuC₆H₂O)₂Ti(CH₂Ph)₂ (Cat 3)

This compound corresponds to Formula (I) with X¹=X²=benzyl having as the alkoxide ligand the ligand of formula (II), wherein n=0, R¹=R²=tertiary butyl and R³=R⁴=methoxy.

114 mg (0.275 mmol) Ti(CH₂Ph)₄ in 5 ml toluene was added to a suspension of 99 mg (0.275 mmol) 2,2'-bis(3-t-butyl-5-methoxyphenol) in 5 ml toluene. After stirring for 16 hours at 20 °C the toluene was removed in vacuo. This afforded a purple coloured oil which could be crystallized from hexane or ether at -40 °C to give red block-like crystals.

Polymerization experiments

In table 1 ethene polymerization results for several titanium and zirconium compounds are listed. In each polymerization experiments the following conditions were applied:

- ethylene pressure: 3 bar
- polymerization temperature: 20 °C, except for the catalyst of Example 4, Cat 1 and Cat 3, where the polymerization temperature was 40 °C
- 0.02 mmol catalyst
- 5 mmol methylaluminoxane as a 10% solution in toluene
- 200 ml toluene
- polymerization time: 15-30 minutes, except for Cat 3, where the polymerization time was 1.5 hours

Table 1

Ethene polymerization					
Catalyst of	Rate (kg/g M/hr)	M _w	M _n	PD	m.p. (°C)
Example 1	8.5	2x10 ⁵	8300	24	125
Example 2	2.3	3.6x10 ⁵	24000	15	120
Example 3	3.3				133
Example 4	2.0	4.2x10 ⁵	39000	10.5	133
Example 5	9.2				133
Example 9	0.53				
Cat 1	10.4	3.4x10 ⁵	50000	7.0	117
Cat 2	2.8				
Cat 3	0.38				

In the above table M_w is weight average molecular weight, M_n is number molecular weight and PD stands

for polydispersity and is equal to M_w/M_n . Molecular weight data were determined by GPC. The melting point (m.p.) of the polyethylene obtained was determined by DSC.

Example 11

The catalyst of Example 1 was also used for the polymerization of propene. At a polymerization temperature of 45 °C, a propene pressure of 6 bar and a polymerization time of 60 minutes -all other conditions are equal to those applied during ethene polymerization- the following data were obtained.

Rate : 0.43 (kg/g Zr/hr)

M_w : 1.2×10^6

M_n : 7600

PD : 15.8

Example 12

To 0.02 mmol of the catalyst of Example 5 in 200 ml toluene were added 200 equivalents of $HC \equiv CR$ at 20 °C, with R as defined in table 2. The trimerization was complete within 5 minutes at 20 °C. The same experiment was performed using the catalyst of Example 8.

The results are listed in table 2.

Table 2

Cyclic trimerization of $HC \equiv CR$		
Catalyst of	R	Ratio 1,2,4 : 1,3,5
Example 5 ($R^1=R^2=SiMePh_2$)	$SiMe_3$	1 : 1
	phenyl	1 : 1
	p-tolyl	1 : 1
Example 8 ($R^1=R^2=SiPh_3$)	$SiMe_3$	4 : 1
	phenyl	4 : 1
	p-tolyl	4 : 1

From table 2 it is clear that the use of more bulky substituents R^1 and R^2 ($SiPh_3$ as compared to $SiMePh_2$) disfavour the formation of the 1,3,5-trisubstituted benzene.

Example 13

1-hexene polymerisation

Ca. 2×10^{-6} mol catalyst was dissolved in 5 ml 1-hexene at 20 °C in the drybox. A ca. 100 fold excess of MAO was added as a solution in 3 ml toluene. The homogeneous solution formed was stirred for 16 h at 20 °C. The reaction vessel was then removed from the drybox and MeOH and then 1 M HCl added to destroy excess MAO. The toluene solution was decanted and evaporated. Identification of polyhexene was performed by 1H and ^{13}C NMR spectroscopy, and GPC analysis. The molar mass was determined by GPC. For NMR analysis the polymer was dissolved in $CDCl_3$. The endgroups were identified by APT experiments and fully coupled ^{13}C NMR. DSC analysis (-40 °C * 100 °C) shows no T_g or T_m .

Table 3 lists the results of the hexene polymerization runs with reference to the catalysts mentioned hereinbefore.

Table 3

1-hexene polymerization			
Catalyst	Results		
Catalyst 3	oligomers	Mw = 290	P.D. = 1.21
Catalyst 1	polyhexene	Mw = 19000	P.D. = 1.71
Example 2	polyhexene	Mw = 670000	P.D. = 2.23
Example 5	polyhexene	-	-
Example 8	polyhexene	-	-
Example 6	oligomers	-	-

1,3-butadiene polymerization

A 25 ml autoclave was charged with 2×10^{-5} mol catalyst, a 100 fold excess of MAO and 15 ml toluene. It was pressurized with 1.5 bar butadiene at 20 °C. After 3 h the autoclave was opened and the excess MAO destroyed by addition MeOH and 1 M HCl. Decanting the organic layer and evaporating the solvents yielded polybutadiene as a rubber-like polymer. The structure was identified by ^1H and ^{13}C NMR spectroscopy. The ratio between 1,2-methylene and 1,4-cis/trans units was determined by ^1H NMR spectroscopy. To dissolve the polymer it was refluxed in $\text{C}_2\text{D}_2\text{Cl}_4$ for 1 h under an inert atmosphere. 1,2-methylene units resonate at 4.8 and 1.3 ppm, 1,4-trans units at 1.98 and 5.4 ppm, and 1,4-cis units at 5.32 and 2.03 ppm. The ratio can be calculated from the integral of the individual peaks. E.R. Santee, Jr., R. Chang and M. Morton Polymer Lett. Ed. 1973, 11, 453.

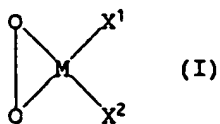
Table 4 lists the results of the butadiene polymerization runs referring to the catalysts mentioned before.

Table 4

Butadiene polymerization		
Catalyst	Results	
Catalyst 3	polybutadiene,	mixture of 30% 1,2-vinyl, cis/trans-1,4
Catalyst 1	polybutadiene	-
Example 2	polybutadiene	no 1,2-vinyl, cis/trans-1,4
Example 5	polybutadiene	-
Example 8	polybutadiene	no 1,2-vinyl, 50/50 cis/trans-1,4
Example 6	polybutadiene	7% 1,2-vinyl, 7% trans-1,4, 81% cis-1,4

Claims

1. A process for the polymerization or oligomerization of olefinically or acetylenically unsaturated hydrocarbons in the presence of a homogeneous catalyst characterized in that the latter is a compound of general formula (I)

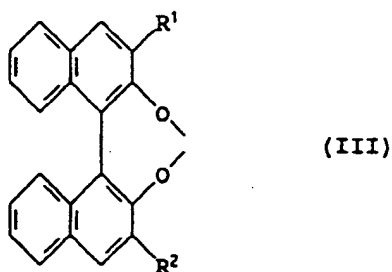
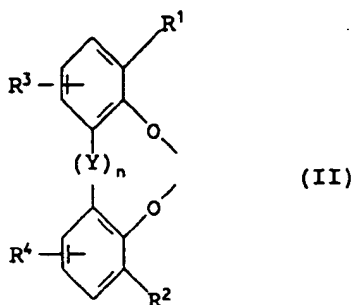


wherein:

- M is Ti or Zr;
- X¹ and X² independently represent halogen, an optionally substituted aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms, a silyl group or an alkoxy group of general formula -OR' with R' being an aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms;



represents a chelating alkoxide ligand of general formula (II) or (III):



wherein:

- R¹ and R² independently represent a sterically hindering alkyl group or an alkoxy group of general formula OR' with R' as previously defined, or a silyl group of general formula SiRᵃRᵇRᶜ with Rᵃ, Rᵇ and Rᶜ independently representing a lower alkyl group, an aryl group, an arylalkyl group or an alkylaryl group;
- R³ and R⁴ independently represent hydrogen, an optionally substituted aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms, a silyl group or an alkoxy group of general formula OR' with R' as previously defined;
- Y is a divalent bridging group selected from the group consisting of methylene, ethylene, -S- and -O-; and
- n is 0 or 1,

2. A process according to claim 1, wherein the unsaturated hydrocarbon is ethene or propene and the polymerization is effected in the presence of an organo aluminium cocatalyst.

3. A process according to claim 1, comprising the cyclic trimerization of a terminal acetylene having the formula (IV):



wherein R represents a hydrocarbyl silyl group, an optionally substituted aryl group or an alkyl group of 1 to 20 carbon atoms other than a tertiary alkyl.

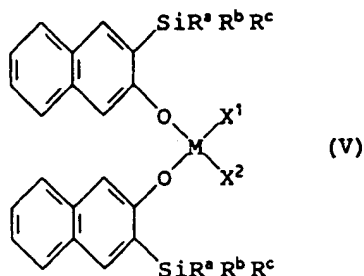
4. A process according to any one of claims 1 to 3, wherein X^1 and X^2 in formula (I) are the same and selected from the group consisting of halogen, alkylene trialkyl silyl, aryl, alkylaryl, arylalkyl and lower alkyl.

5. A process according to any one of claims 1 to 4, wherein R^1 and R^2 are the same and represent a sterically hindering alkyl group of 4 to 10 carbon atoms.

6. A process according to any one of claims 1 to 5, wherein R^3 and R^4 are located on the meta-position in relation to R^1 and R^2 respectively.

7. A process according to claim 6, wherein R^3 and R^4 are the same and represent methoxy, methyl or ethyl.

8. Novel compound of general formula (V):



wherein:

- M is Ti or Zr;
- X^1 and X^2 independently represent halogen, an optionally substituted aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms, a silyl group or an alkoxy group of general formula $-\text{OR}'$ with R' being an aliphatic or aromatic hydrocarbon group of 1 to 20 carbon atoms; and
- R^a , R^b and R^c independently represent a lower alkyl group, an aryl group, an arylalkyl group or an alkylaryl group.

9. Compound according to claim 8, wherein X^1 and X^2 are selected from the group consisting of chlorine, benzyl, methylene trimethyl silyl and methyl.

10. Compound according to any one of claims 8 to 9, wherein R^a , R^b and R^c are selected from methyl and phenyl.

11. Compound according to any one of claims 8 to 10, wherein: $\text{M}=\text{Zr}$ or Ti , $\text{R}^a=\text{R}^b=\text{R}^c$ =independently methyl or phenyl and $\text{X}^1=\text{X}^2=\text{Cl}$ or benzyl or methyl.

12. Compound according to any one of claims 8 to 10, wherein: $\text{M}=\text{Zr}$, $\text{R}^a=\text{R}^b=\text{R}^c$ =phenyl and $\text{X}^1=\text{X}^2$ =methylene trimethyl silyl.